Acta Cryst. (1973). B29, 1594

The Structure and Electron Density of Ethyleneimine Quinone

BY TETSUZO ITO AND TOSIO SAKURAI

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama, Japan

(*Received* 10 *January* 1973; *accepted* 14 *March* 1973)

The crystal structure of ethyleneimine quinone, 2,5-bis(ethyleneimino)-1,4-benzoquinone, $C_6H_2O_2(NC_2H_4)_2$, has been investigated at three different temperatures, 300 ± 5, 240 ± 10 and 110 ± 20°K. The crystal structures at the three temperatures are essentially the same. The crystal is triclinic, space group $P\bar{1}$ with $Z=1$. The three-membered ring of the ethyleneimino group is approximately a regular triangle with N–C = 1·469, 1·475, C–C = 1·498 Å, C–N–C = 61·2, N–C–C = 59·2 and 59·6°. Difference electron density maps through the three-membered ring revealed bonding electrons outside the triangle, in conformity with the theoretical prediction of the bent bond.

Introduction

The three-membered rings of cyclopropyl, ethyleneimino and ethyleneoxido groups are typical examples of highly strained structures. Coulson & Moffit (1949) proposed the bent-bond model for cyclopropane on the basis of a valence bond treatment of the system; the bonding electrons are not centred on the C–C line but are displaced outside of the triangle, forming the bent bond. Recent SCF-LCAO-MO calculations have also revealed the bent-bond nature of these three-membered ring systems (Kochanski & Lehn, 1970; Bonaccorsi, Scrocco & Tomasi, 1970). The crystal structure analyses of 2,5-dimethyl-7,7-dicyanonorcaradiene by Fritchie (1966), and of *cis*-1,2,3-tricyanocyclopropane by Hartman & Hirshfeld (1966) have experimentally confirmed the validity of the bent-bond model by virtue of the electron distributions around the cyclopropyl group of the molecules.

Recently, the electron density distribution of the ethylene oxide ring was studied for tetracyanoethylene oxide by X-ray and neutron diffraction (Matthews & Stucky, 1970).

In order to investigate the electron distribution around an ethyleneimino group, the crystal structure analysis of ethyleneimine quinone, 2,5-bis(ethyleneimino)-1,4-benzoquinone, $C_6H_2O_2(NC_2H_4)_2$, was undertaken at room temperature and two lower temperatures (Ito & Sakurai, 1972). This compound seemed especially suitable for the present purpose, because preliminary experiments indicated that the crystal structure is simple ($P\bar{1}$ and $Z=1$), and no phase transition was observed throughout the observed temperature range. Difference electron density maps through the three-membered ring revealed bonding electrons outside the triangle, in accordance with the theoretical prediction of the bent bond.

Experimental

Crystal data

2,5-Bis(ethyleneimino)-1,4-benzoquinone, $C_6H_2O_2(NC_2H_4)_2$; F.W. 190·20.

Triclinic prismatic along the c axis;

	300 ± 5 °K	240 ± 10 °K	110 ± 20°K
a	6·889 (7) Å	6·856 (4) Å	6·810 (4) Å
b	8·468 (6)	8·434 (3)	8·396 (3)
c	3·931 (3)	3·919 (3)	3·863 (2)
α	94·62 (7)°	94·10 (5)°	93·77 (4)°
β	100·13 (10)	99·66 (12)	99·35 (11)
γ	89·56 (8)	89·86 (4)	89·93 (6)
V	225·0 (3)	222·8 (2)	217·5 (2) Å^3
d_x (g cm^{-3})	1·404	1·417	1·452

$Z=1$ from volume considerations.
Space group $P\bar{1}$ from a statistical test.
Linear absorption coefficient for Mo $K\alpha$ radiation $\mu=1{\cdot}22$ cm^{-1}.

Ethyleneimine quinone powder was prepared by dropwise addition of ethyleneimine to an ethanolic solution of *p*-benzoquinone (Gauss & Petersen, 1955). Orange prismatic crystals elongated along the c axis were obtained by recrystallization of the powder from benzene or acetone solutions.

The cell dimensions were determined from the sin θ values of about thirty reflexions around the c axis, measured with an automatic diffractometer of equi-inclination type, READ-1 (Sakurai, Ito & Iimura, 1970). The wavelength used was 0·71069 Å for Mo $K\alpha$ radiation. The number of molecules per unit cell was found to be unity from a comparison of the cell volume of ethyleneimine quinone, 225·0 Å^3 at 300°K, with those of similar crystals; for example, $V=414{\cdot}8$ Å^3 with $Z=2$ for tetrachloro-*p*-benzoquinone (Chu, Jeffrey & Sakurai, 1962). The $N(z)$ test (Howells, Phillips & Rogers, 1950) clearly showed that the crystal is centric $P\bar{1}$.

Low temperatures

The low temperatures were obtained with a Cryo-Tip refrigerator (Air Products & Chemicals). The refrigerator produces low temperatures by means of high-pressure nitrogen gas. The goniometer head of the diffractometer was specially designed to support the metal end of the refrigerator; the refrigerator was originally

designed so that the vacuum shield end could be fixed to the goniometer head. This revision of installation minimized possible displacements of a sample crystal during measurements and allowed the use of a very thin glass vacuum shield with low background scattering of X-rays.

The temperature of a sample was measured with a copper-constantan thermocouple embedded in the copper block of the refrigerator. The measured temperature was calibrated with hexamine crystal as a standard. The lattice constants of hexamine given by Becka & Cruickshank (1963) were used for the calibration; $a(298\,°K) = 7{\cdot}021$ (9) and $a(100\,°K) = 6{\cdot}931$ (9) Å. It was found that the temperatures of the sample were higher than those detected by the thermocouple by 13 and 33° at 240 and 110 °K respectively. The temperatures as detected by the thermocouple were kept constant within ±5° during measurements.

Intensity measurements

The intensities were measured with the automatic diffractometer READ-1 and Mo Kα radiation monochromated with a graphite monochromator of high mosaicity (Union Carbide). Two crystals were used for the measurements; one from benzene and another from acetone solutions were used at 300 and at 240 and 110 °K, respectively. Both crystals were about 1 mm long along the c axis with cross sections of about $0{\cdot}25 \times 0{\cdot}35$ mm. Reflexions around the c axis up to the 5th levels were explored; control measurements around the a axis at room temperature showed no significant deviations of interlevel scales from unity. The crystals were rotated in the ω-scan mode with a scanning speed of 1° per min. The scan widths were so chosen as to be proportional to the peak widths (Ito, 1971). The diffracted X-rays were detected with a NaI scintillation counter and analysed with a pulse-height analyser. Strong diffraction beams were attenuated to within the linear range of the counter (below 4200 c.p.s.) by inserting zirconium foils with known attenuation factors.

Altogether 503, 773 and 895 independent reflexions were obtained at 300, 240 and 110 °K, respectively. These were corrected for Lorentz and polarization effects. Absorption corrections were not applied because they were negligible ($\mu r \sim 0{\cdot}02$). Extinction effects were found to be insignificant because no appreciable systematic discrepancies between F_o and F_c were observed during the refinement.

Determination of the structure

The structure was first solved using the data collected at 300 °K. The space group $P\bar{1}$ with $Z=1$ requires that the ethleneimine quinone molecule be located on the inversion centre. One half of the molecule, ONC_5H_5, constitutes the asymmetric unit of the cell. The exceptionally high F_o values of the 111 and 011 reflexions suggested that the quinone ring, C(1), C(2) and C(3), including O(1) and N(1) bonded to it, lies approximately on these planes. Therefore, a Patterson 111 section was calculated and approximate coordinates of the above atoms were easily obtained from analysis of the section. Coordinates of the two ethyleneimino carbons were obtained from a Fourier map. The structure was then refined by block-diagonal least-squares calculations. After several cycles of isotropic and anisotropic refinement, the R value was 7·8%. At this stage, a difference electron density map clearly revealed all the hydrogen atoms. Several additional cycles of full-matrix least squares including the hydrogen atoms with isotropic temperature factors converged to the final R value of 4·1%.

The structures at 240 and 110 °K could be refined starting from the results at 300 °K. The final R values were 3·9 and 3·5%, respectively. No phase transition was observed within the observed temperature range.

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2) *with standard deviations*

The B values for the non-hydrogen atoms are the equivalent isotropic temperature factors proposed by Hamilton (1959).

300 °K	x/a	y/b	z/c	B
O(1)	1968 (4)	−2662 (3)	−990 (8)	3·6
N(1)	1855 (4)	2565 (3)	4334 (8)	2·8
C(1)	1059 (5)	1288 (4)	2152 (9)	2·3
C(2)	1999 (5)	−80 (4)	1676 (10)	2·6
C(3)	1080 (4)	−1435 (4)	−459 (10)	2·4
C(4)	2144 (5)	4110 (4)	3012 (11)	3·2
C(5)	3869 (5)	3121 (4)	4332 (11)	3·3
H(1)	3351 (47)	−203 (38)	2648 (86)	3·2 (7)
H(2)	1815 (44)	4189 (36)	322 (82)	2·7 (7)
H(3)	1744 (47)	4991 (39)	4261 (88)	3·4 (8)
H(4)	4592 (51)	2538 (42)	2496 (94)	4·2 (8)
H(5)	4621 (47)	3419 (39)	6754 (88)	3·4 (8)
240 °K				
O(1)	1983 (2)	−2667 (2)	−970 (4)	2·6
N(1)	1842 (2)	2571 (2)	4364 (4)	1·9
C(1)	1053 (3)	1289 (2)	2159 (4)	1·6
C(2)	2011 (3)	−82 (2)	1694 (5)	1·9
C(3)	1083 (3)	−1446 (2)	−465 (5)	1·7
C(4)	2134 (3)	4117 (2)	3007 (5)	2·2
C(5)	3863 (3)	3128 (2)	4374 (6)	2·5
H(1)	3381 (31)	−230 (26)	2711 (55)	2·3 (5)
H(2)	1759 (33)	4172 (27)	379 (58)	2·7 (5)
H(3)	1772 (32)	5044 (26)	4416 (57)	2·7 (5)
H(4)	4586 (33)	2565 (27)	2573 (58)	3·0 (5)
H(5)	4657 (34)	3378 (28)	6674 (61)	3·3 (5)
110 °K				
O(1)	2007 (2)	−2680 (1)	−946 (3)	1·1
N(1)	1817 (2)	2576 (2)	4397 (3)	0·8
C(1)	1041 (2)	1291 (2)	2181 (4)	0·7
C(2)	2020 (2)	−87 (2)	1728 (4)	0·8
C(3)	1095 (2)	−1450 (2)	−452 (4)	0·7
C(4)	2123 (2)	4138 (2)	3012 (4)	0·9
C(5)	3861 (2)	3139 (2)	4411 (4)	1·0
H(1)	3396 (28)	−215 (23)	2866 (50)	1·0 (4)
H(2)	1761 (30)	4180 (25)	389 (53)	1·4 (4)
H(3)	1744 (30)	5051 (24)	4354 (53)	1·4 (4)
H(4)	4603 (30)	2580 (25)	2709 (54)	1·6 (4)
H(5)	4640 (29)	3408 (24)	6793 (52)	1·3 (4)

Attempts to refine the anisotropic temperature factors of the hydrogen atoms turned out to be unsuccessful; the thermal ellipsoids of some hydrogens were extraordinarily elongated (at 300°K), or some led to nonpositive definiteness (at 240 and 110°K).

The final atomic coordinates and thermal parameters are given in Tables 1 and 2 respectively. The observed and calculated structure factors are compared in Table 3. The atomic scattering factors for the non-hydrogen atoms were taken from *International Tables*

Table 2. *Thermal parameters with standard deviations*

The thermal parameters refer to the expression:

$$T=\exp\left[-10^{-4}.2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*+\ldots)\right].$$

300°K	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	352 (13)	310 (13)	670 (21)	84 (10)	49 (13)	−74 (13)
N(1)	321 (14)	285 (14)	430 (21)	−43 (11)	30 (14)	40 (14)
C(1)	282 (16)	285 (16)	332 (22)	−29 (13)	53 (17)	59 (16)
C(2)	245 (16)	292 (16)	413 (24)	1 (13)	−23 (16)	21 (17)
C(3)	277 (17)	263 (16)	377 (23)	9 (13)	72 (17)	25 (16)
C(4)	422 (20)	249 (16)	545 (28)	−41 (14)	98 (20)	33 (18)
C(5)	326 (19)	404 (20)	521 (28)	−84 (15)	24 (19)	28 (20)
240°K						
O(1)	273 (7)	229 (7)	483 (9)	66 (6)	44 (6)	−34 (6)
N(1)	248 (7)	211 (7)	253 (8)	−43 (6)	25 (6)	−13 (6)
C(1)	208 (8)	201 (8)	210 (9)	−29 (7)	38 (7)	11 (7)
C(2)	206 (8)	219 (8)	296 (9)	−1 (7)	−3 (7)	2 (7)
C(3)	218 (8)	204 (8)	241 (9)	−9 (7)	40 (7)	15 (7)
C(4)	326 (10)	201 (9)	328 (10)	−55 (7)	73 (8)	−7 (7)
C(5)	248 (9)	298 (10)	374 (11)	−72 (8)	30 (8)	−8 (9)
110°K						
O(1)	126 (5)	103 (5)	179 (5)	23 (4)	25 (4)	−2 (4)
N(1)	105 (5)	85 (5)	117 (6)	−17 (4)	18 (4)	2 (4)
C(1)	87 (6)	107 (6)	81 (6)	−11 (5)	19 (5)	5 (5)
C(2)	80 (6)	103 (6)	117 (6)	−6 (5)	−4 (5)	−6 (5)
C(3)	94 (6)	85 (6)	95 (6)	−6 (5)	25 (5)	6 (5)
C(4)	128 (6)	92 (6)	141 (7)	−17 (5)	34 (5)	5 (5)
C(5)	103 (6)	114 (7)	144 (7)	−29 (5)	9 (5)	−8 (5)

Table 3. *Observed and calculated structure factors* (×20) (*a*) 300°K (503 reflexions)

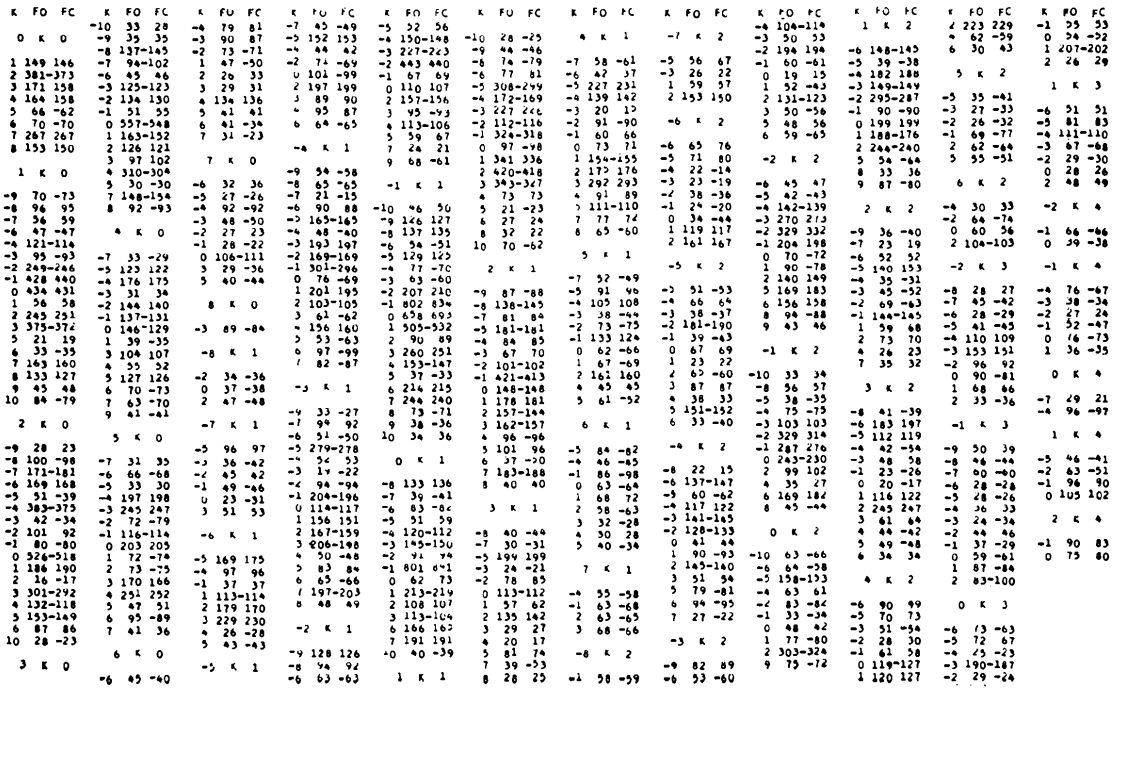
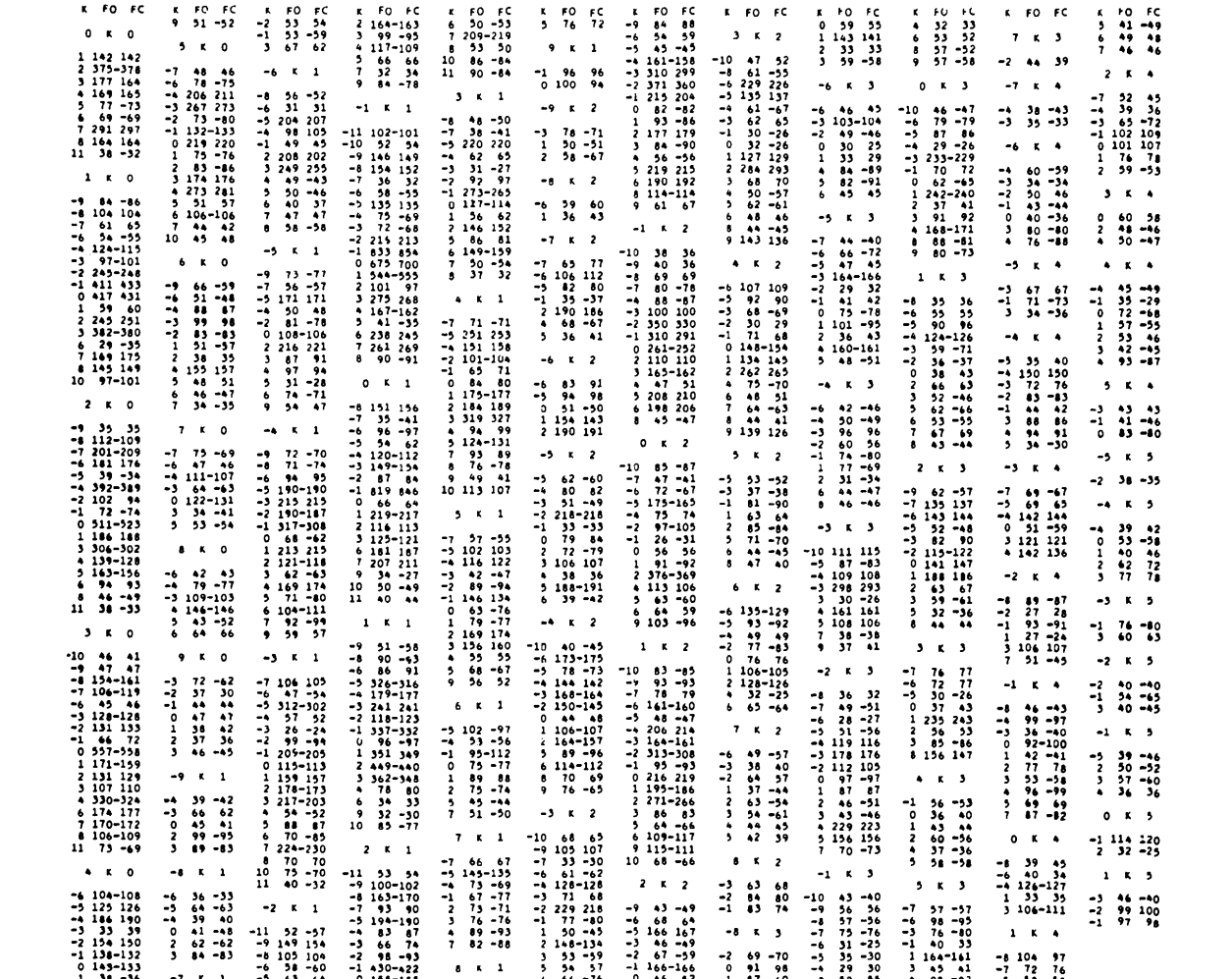


Table 3 (*cont.*) (*b*) 240°K (773 reflexions)



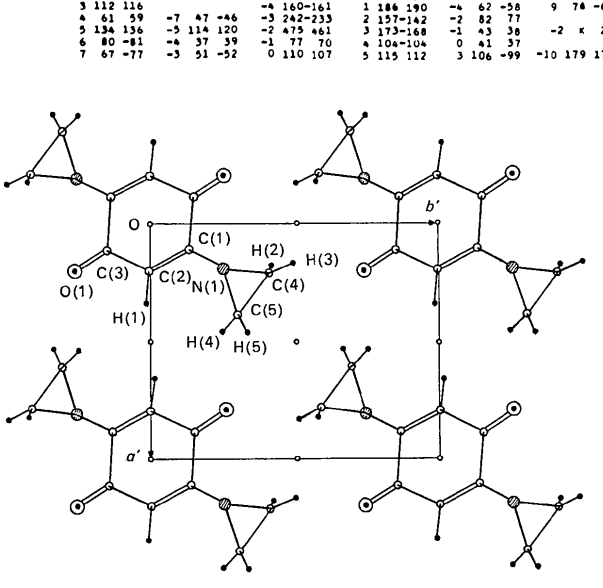


Fig. 1. Structure of ethleneimine quinone viewed down the *c* axis. **c** is out of the plane of the paper.

for X-ray Crystallography (1962). Those for a free hydrogen atom listed in the Table were found to be inappropriate in the present case, because the *B* values of the hydrogen atoms were systematically smaller than those of the carbon atoms to which they are bonded; moreover, all of them became negative at 110°K. Therefore, the atomic scattering factors for a hydrogen atom in a hydrogen molecule (Stewart, Davidson & Simpson, 1965) were used with better results. The average difference between the two corresponding *B* values was about 2·0 Å².

Results and discussion

Crystal structure

The crystal structures of ethyleneimine quinone at 300, 240 and 110°K are essentially the same. The structure viewed down the *c* and *a* axes is shown in Figs. 1 and 2, respectively. The molecules lie approximately on

Table 3 (*cont.*) (*c*) 110°K (895 reflexions)

K	FO	FC
0 K 0		
1	135	134
2	380	-377
3	184	175
4	180	175
5	89	-89
6	70	-67
7	348	354
8	182	183
11	48	-45
1 K 0		
-9	117	-124
-8	119	122
-7	75	81
-6	73	-72
-4	127	-122
-3	106	-111
-2	248	-253
-1	415	428
0	420	433
1	69	66
2	245	252
3	399	-399
4	32	33
5	28	28
6	42	-43
7	201	200
8	185	194
9	71	66
10	152	-150
2 K 0		
-11	90	-73
-9	54	55
-8	120	-122
-7	254	-274
-6	205	199
-4	428	-426
-3	58	-49
-2	101	93
-1	61	-63
0	529	-534
1	183	186
3	313	-310
4	150	-139
5	179	-172
6	108	104
8	63	-56
11	58	-53
3 K 0		
-10	64	66
-9	63	66
-8	193	-204
-7	129	-144
-6	62	55
-3	143	-140
-2	132	133
-1	99	101
0	584	-586
1	189	-178
2	143	142
3	124	128
4	377	-369
6	211	209
7	203	-211
8	138	-143
11	121	-119
4 K 0		
-6	134	-136
-5	133	137
-4	217	222
-3	45	47
-2	178	180
-1	153	-145
0	154	-141
1	42	-41
3	130	137
4	60	63
5	149	151
6	97	-97
7	75	-82
9	74	-76
5 K 0		
-10	83	77
-9	39	-37
-7	66	75
-6	95	-90
-4	232	234
-3	335	344
-2	75	-79
-1	173	-173
0	261	257
1	70	-82
2	103	-104
3	194	195
4	337	340
5	65	75
6	134	-135
7	62	62
6 K 0		
-9	111	-107
-6	80	-78
-4	95	103
-3	128	129
-2	102	-106
1	63	-66
2	37	39
4	205	209
5	71	79
6	68	-66
7	56	-55
9	44	51
7 K 0		
-7	148	-136
-6	73	71
-4	149	-145
-3	93	-96
0	169	-180
3	52	-60
5	78	-72
7	45	-49
8 K 0		
-6	82	77
-5	40	-33
-4	94	-93
-3	174	-164
-1	55	52
0	41	-49
1	43	-38
4	224	-223
5	75	-84
6	115	112
9 K 0		
-3	116	-109
-2	49	54
-1	63	61
0	75	77
1	65	63
2	66	64
3	56	-53
-9 K 1		
-4	49	-52
-3	109	107
-2	83	-86
0	71	69
2	168	-165
3	126	-122
-8 K 1		
-5	99	-101
-4	64	60
-3	55	-56
-2	58	-63
0	66	-69
2	108	-104
3	109	-108
-7 K 1		
-8	59	-67
-7	69	-73
-6	55	56
-5	173	175
-3	84	-82
-2	87	85
-1	74	-83
0	47	-50
3	83	87
6	42	-44
-6 K 1		
-8	74	-74
-6	48	47
-5	273	280
-4	116	120
-1	63	57
1	158	-160
2	280	277
3	302	310
4	75	-79
5	55	-52
6	57	58
7	60	59
8	104	-101
9	72	72
-5 K 1		
-9	112	-119
-7	60	-65
-5	205	206
-4	65	61
-2	99	-98
0	123	-121
2	263	273
3	89	88
4	112	112
5	36	-31
6	82	-88
9	87	87
-4 K 1		
-9	106	-108
-8	93	-96
-6	105	106
-5	234	-239
-4	36	-36
-3	254	252
-2	228	-224
-1	348	-339
0	53	-48
1	236	241
2	153	-151
3	62	-58
4	205	206
5	110	-116
6	120	-125
7	116	-122
9	79	82
-3 K 1		
-11	43	40
-9	49	-50
-8	38	-42
-7	124	127
-6	56	-60
-5	358	-353
-4	64	57
-2	105	-101
-1	217	-216
0	115	-113
1	164	160
2	207	-201
3	231	-215
4	52	-56
5	106	101
6	103	-115
7	276	-285
8	110	109
10	121	-113
-2 K 1		
-11	77	-81
-10	39	-39
-9	219	221
-8	128	132
-6	67	-59
-5	78	85
-4	177	-177
-3	259	-252
-2	514	500
-1	85	78
0	109	108
2	176	-172
3	110	-101
4	119	-110
5	70	74
7	48	55
9	121	-119
11	51	-46
-1 K 1		
-11	159	-160
-10	63	69
-9	203	203
-8	180	182
-7	41	39
-6	70	-67
-5	153	155
-4	76	-63
-3	83	-81
-2	229	222
-1	853	883
0	669	702
1	562	-578
2	130	120
3	284	278
4	188	-177
5	37	-31
6	286	297
7	305	311
8	123	-130
10	60	61
0 K 1		
-8	197	197
-7	42	-41
-6	128	-126
-5	63	71
-4	128	-118
-3	157	-161
-2	74	75
-1	806	842
0	57	58
1	218	-216
2	113	109
3	139	-133
6	207	217
7	237	242
9	38	-37
10	70	-70
11	79	79
1 K 1		
-11	42	41
-10	35	-31
-9	82	-79
-8	119	-125
-6	116	124
-5	366	-356
-4	210	-206
-3	273	272
-2	131	-134
-1	362	-354
0	96	-99
1	368	365
2	472	-467
3	376	-361
4	87	88
6	56	31
9	52	-48
10	97	-97
2 K 1		
-11	88	88
-9	129	-134
-8	213	-225
-7	117	113
-5	219	-217
-4	98	98
-3	76	78
-2	86	-83
-1	448	-435
0	182	-180
1	201	206
2	150	-137
3	187	-180
4	122	-121
5	139	133
6	59	-67
7	257	-268
8	67	69
10	129	-128
11	137	-137
3 K 1		
-11	56	54
-8	56	-54
-7	61	-54
-5	262	268
-4	84	84
-3	34	-37
-2	121	119
-1	293	-284
0	127	-124
1	58	63
2	163	173
3	36	39
5	100	96
6	172	-188
7	63	-65
8	40	38
4 K 1		
-7	83	-87
-5	299	302
-4	193	197
-3	35	28
-2	126	-130
-1	82	81
0	108	106
1	215	-214
2	205	212
3	372	381
4	114	119
5	160	-162
7	122	117
8	114	-113
9	73	66
10	174	166
5 K 1		
-9	70	-58
-8	61	67
-7	81	-79
-6	40	-39
-5	126	124
-4	145	150
-3	48	-50
-2	122	-128
-1	171	160
0	71	-86
1	100	-98
2	188	193
3	182	191
4	77	83
5	91	-87
9	66	64
6 K 1		
-8	70	-65
-6	49	45
-5	139	-138
-4	90	-90
-1	123	-142
0	102	-109
1	116	118
2	104	-106
3	36	-45
4	54	51
5	56	-60
6	59	-59
7	79	-72
7 K 1		
-7	126	120
-5	204	-200
-4	103	-97
-1	104	-103
2	91	-89
3	106	-104
4	139	-143
5	68	70
8 K 1		
-4	94	-91
-2	129	125
-1	51	53
0	55	61
3	149	-147
4	55	-46
5	126	121
9 K 1		
0	176	168
-9 K 2		
-3	128	-132
-2	42	-42
0	48	-47
1	87	-86
2	106	-106
-8 K 2		
-6	103	107
-5	61	68
-4	78	-75
-2	51	51
-1	138	-141
1	68	72
-7 K 2		
-7	128	133
-6	173	177
-5	109	107
-4	45	-49
-3	58	58
-1	54	-54
1	104	103
2	265	264
4	95	-96
5	70	71
7	49	-43
-6 K 2		
-8	56	56
-6	127	120
-5	142	142
-3	33	-33
-2	48	-47
0	60	-62
1	200	197
2	236	240
3	49	-56
6	35	-28
8	73	75
-5 K 2		
-5	77	-73
-4	112	115
-3	76	-76
-2	276	-274
0	104	107
2	102	-106
3	151	151
4	37	34
5	257	-264
8	56	51
-4 K 2		
-10	69	-69
-6	233	-236
-5	101	-96
-4	185	183
-3	199	-198
-2	170	-169
0	47	51
1	137	-139
2	189	-183
3	73	83
5	111	-116
6	142	-142
7	33	-29
8	92	95
9	110	-106
-3 K 2		
-10	109	103
-9	156	155
-6	61	-57
-4	153	-155
-3	108	104
-2	264	257
-1	107	-109
1	51	-45
2	165	-150
3	69	-71
5	65	67
6	95	-100
7	47	56
9	108	-105
-2 K 2		
-10	276	277
-9	127	125
-6	85	88
-5	52	-50
-4	193	-189
-3	355	343
-2	418	407
-1	224	211
0	96	-99
1	84	-77
2	210	209
3	109	-109
4	57	-53
5	270	268
6	231	241
8	155	-155
9	114	114
-1 K 2		
-10	38	39
-9	43	42
-8	108	102
-7	108	-111
-4	106	-105
-3	94	90
-2	367	348
-1	331	316
0	287	-283
2	118	117
3	181	-178
4	67	63
5	244	250
6	233	242
8	49	-45
10	43	-42
0 K 2		
-10	143	-146
-7	51	-54
-6	90	-83
-5	202	-195
-4	97	97
-3	27	-30
-2	140	-144
-1	25	-27
0	70	73
1	118	-112
2	420	-413
3	37	38
4	120	114
5	90	-86
6	66	71
8	39	-32
9	140	-141
1 K 2		
-10	122	-126
-9	139	-142
-7	115	122
-6	203	-199
-5	72	-68
-4	261	264
-3	180	-178
-2	353	-347
-1	105	-104
0	248	248
1	209	-200
2	297	-288
3	100	95
5	78	-79
6	134	-148
8	58	62
9	167	-154
10	108	-107
2 K 2		
-9	49	-56
-7	34	36
-6	94	88
-5	210	208
-4	57	-58
-3	44	-45
-2	53	-45
-1	203	-206
0	50	56
1	103	108
2	102	98
4	39	34
6	199	-217
7	68	69
8	41	40
9	60	-58
3 K 2		
-10	113	103
-8	87	-89
-6	292	294
-5	181	181
-4	85	-92
-3	81	82
1	140	143
2	343	352
3	81	83
4	67	-72
5	60	-71
6	75	71
8	66	-61
9	223	216
4 K 2		
-7	47	-49
-6	133	134
-5	119	121
-3	91	-98
-1	110	100
0	199	-203
1	154	161
2	317	323
4	94	-90
6	65	72
7	95	-88
8	75	62
9	196	185
5 K 2		
-7	40	-37
-5	94	-91
-1	112	-118
1	72	75
2	126	-127
3	48	44
5	117	-109
6	66	-63
8	48	46
6 K 2		
-7	89	80
-6	204	-199
-5	157	-152
-4	85	82
-2	101	-109
-1	43	-47
0	120	115
1	138	-138
2	182	-176
4	43	-35
6	111	-105
7 K 2		
-4	46	-43
-3	67	64
-2	99	98
0	42	41
1	52	-51
2	75	-72
3	104	-105
4	79	79
5	76	75
8 K 2		
-2	122	118
-1	127	129
1	53	-44
-8 K 3		
-3	51	53
-2	122	-124
0	168	175
1	86	88
2	49	44
3	67	-60
-7 K 3		
-6	110	111
-4	37	-44
-3	37	-37
-2	36	-41
-1	40	40
0	76	77
1	219	219
2	37	37
3	90	-94
4	60	54
-6 K 3		
-6	80	81
-4	41	-40
-3	153	-154
-2	42	-44
-1	52	55
3	63	63
4	153	-150
5	134	-136
6	97	91
7	39	35
-5 K 3		
-8	59	-56
-7	66	-76
-6	116	-113
-5	78	78
-3	238	-238
-2	54	54
-1	46	54
0	124	-122
1	136	-135
2	67	69
3	33	33
4	235	-241
5	53	-51
-4 K 3		
-7	56	-51
-6	73	-72
-4	40	-43
-3	135	137
-2	50	52
-1	107	-109
1	98	-91
2	59	-55
4	32	36
6	69	-77
7	52	54
8	97	-87
-3 K 3		
-9	67	-65
-7	64	67
-6	44	-43
-5	121	-120
-4	161	157
-3	393	384
-1	27	-20
0	42	47
4	221	224
5	141	137
7	66	-63
9	75	77
-2 K 3		
-7	70	-73
-5	73	-71
-4	124	124
-3	219	211
-2	143	133
0	131	-127
1	121	121
2	67	-61
3	63	-60
4	288	290
5	200	204
7	99	-100
8	68	76
-1 K 3		
-10	70	-72
-9	102	107
-8	98	-90
-7	130	-122
-5	34	-34
-3	79	-84
-2	81	77
-1	28	-24
0	104	-107
1	135	-134
2	129	-133
3	152	150
6	85	81
7	46	-45
8	94	-92
9	87	-84
0 K 3		
-10	92	-86
-6	121	-119
-5	127	123
-3	304	-307
-2	28	-21
-1	103	104
0	75	-78
1	310	-297
2	60	65
3	110	107
4	223	-231
8	124	-121
9	113	-105
1 K 3		
-10	52	-50
-8	70	63
-7	58	51
-6	68	65
-5	127	130
-4	152	-153
-3	77	-76
-2	60	-53
0	67	77
2	64	60
3	56	-59
5	86	-98
6	76	-81
7	113	116
8	65	-64
9	56	-50
2 K 3		
-9	115	-110
-8	36	34
-7	213	211
-6	203	204
-5	82	-83
-3	141	145
-2	163	-167
0	196	195
1	240	235
2	68	76
3	67	-75
8	89	79
3 K 3		
-9	67	-62
-7	99	98
-6	117	115
-5	39	-39
1	316	323
2	72	75
3	125	-122
8	246	239
4 K 3		
-8	68	-66
-3	87	-93
-1	76	-78
0	35	39
1	43	48
2	76	-76
3	37	42
4	70	-67
5	88	-86
7	42	41
5 K 3		
-7	83	-80
-6	177	-175
-5	47	44
-4	34	33
-3	126	-130
-1	51	58
1	251	-248
3	63	68
4	145	-143
5	59	-62
6 K 3		
-5	57	65
-3	62	62
-2	61	69
0	69	-64
1	116	-113
4	65	66
-7 K 4		
-2	39	38
0	55	53
2	54	-57
-6 K 4		
-4	105	-108
-3	60	-53
-2	89	81
-1	98	-92
0	71	-74
3	154	-151
4	148	-144
-5 K 4		
-3	91	92
-1	98	-103
1	50	-44
3	43	-46
-4 K 4		
-7	48	-53
-6	61	-54
-5	76	81
-4	249	246
-3	89	90
-2	135	-136
-1	92	95
1	109	-111
2	50	42
3	153	153
4	128	131
5	61	-62
-3 K 4		
-7	102	-100
-5	82	88
-4	210	209
-3	31	34
0	69	-73
1	30	30
3	177	175
4	210	209
6	56	-48
-2 K 4		
-8	174	-166
-5	43	-46
-3	28	32
-2	39	38
-1	150	-149
0	60	-63
2	34	-33
3	136	139
7	85	-78
-1 K 4		
-8	83	-82
-4	162	-158
-3	69	-64
-2	85	85
-1	81	-98
0	140	-150
1	50	-48
2	121	118
3	116	-113
4	150	-152
5	124	121
6	50	-51
7	149	-144
0 K 4		
-8	77	84
-6	57	53
-4	187	-192
1	45	38
3	144	-148
1 K 4		
-8	168	178
-7	122	125
-5	74	-74
-4	61	62
-2	120	-128
-1	203	210
0	196	199
2	47	-43
5	79	-82
6	97	97
2 K 4		
-7	71	69
-4	67	69
-3	105	-104
-1	141	145
0	152	149
1	121	125
2	89	-87
4	37	37
3 K 4		
-5	42	-47
-4	70	-71
-1	56	-51
0	78	83
2	81	-79
4	71	-74
4 K 4		
-4	78	-87
-3	37	-37
-1	54	-49
0	118	-120
1	96	-91
2	93	90
3	81	-84
4	159	-151
5 K 4		
-2	39	42
-1	56	-62
0	132	-132
-5 K 5		
-1	73	69
0	91	-93
-4 K 5		
-4	56	67
-3	58	-58
-2	57	53
0	94	-95
1	87	91
2	123	124
-3 K 5		
-4	44	50
-2	59	-60
-1	127	-128
0	35	34
3	114	118
-2 K 5		
-5	52	-54
-2	68	-70
-1	106	-112
3	101	-98
-1 K 5		
-5	79	-80
-4	85	-93
-3	77	72
0	35	37
2	85	-90
3	106	-108
0 K 5		
-2	53	59
-1	217	217
1 K 5		
-3	95	-88
-2	169	174
-1	154	164
2 K 5		
-2	41	32
0	78	79
1	42	-44

the $(\bar{1}\bar{1}1)$ planes forming molecular sheets. These sheets are stacked along the *c* axis. The intermolecular interactions between the adjacent sheets as well as within a sheet are van der Waals contacts.

The closest intermolecular distances are summarized in Table 4. These values can be regarded as normal compared with the sums of the van der Waals radii of the atoms; O···C=3·4, N···C=3·5, C···C=4·0, O···H =2·6, N···H=2·7, C···H=3·2 and H···H=2·4 Å (Pauling, 1960). It should be noted that intermolecular distances decrease with decreasing temperatures probably because of the decreasing thermal vibrations of the molecules (see the last column of Table 4).

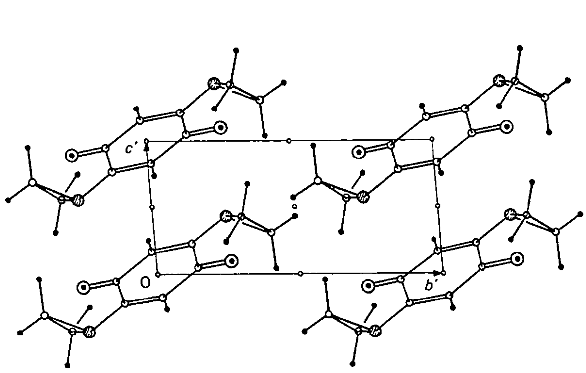


Fig. 2. Structure of ethyleneimine quinone viewed down the *a* axis. **a** is out of the plane of the paper.

Table 4. *Intermolecular van der Waals distances* (Å)

The primes denote the inversions at the origin. The σ_L are the e.s.d.'s of the least-squares results.

	300° K	240° K	110° K	r(300° K)–r(110° K)
O(1)···C(4, $-b$)	3·253	3·216	3·159	0·094
O(1)···C(5′, $+a$)	3·366	3·352	3·319	0·047
O(1)···C(4, $-b-c$)	3·479	3·479	3·440	0·039
O(1)···C(5′, $+a+c$)	3·568	3·551	3·502	0·066
N(1)···C(1, $+c$)	3·471	3·439	3·381	0·090
N(1)···C(4, $+c$)	3·527	3·515	3·470	0·057
N(1)···C(3′, $+c$)	3·594	3·547	3·479	0·115
C(5)···C(5′, $+a+b+c$)	3·514	3·491	3·461	0·053
C(2)···C(3, $+c$)	3·542	3·512	3·451	0·091
C(4)···C(5′, $+a+b+c$)	3·582	3·567	3·540	0·042
C(1)···C(2′, $+c$)	3·689	3·649	3·580	0·109
C(1)···C(1′, $+c$)	3·728	3·682	3·617	0·111
O(1)···H(4′, $+a$)	2·55	2·54	2·51	0·04
O(1)···H(3, $-b-c$)	2·60	2·54	2·53	0·07
O(1)···H(5′, $+a+c$)	2·73	2·71	2·66	0·07
O(1)···H(2, $-b$)	2·76	2·76	2·73	0·03
N(1)···H(2, $+c$)	2·63	2·64	2·61	0·02
C(4)···H(2, $+c$)	2·92	2·94	2·90	0·02
C(5)···H(2, $+c$)	3·03	3·04	2·99	0·04
C(4)···H(5′, $+a+b+c$)	3·05	3·04	3·01	0·04
C(4)···H(3′, $+b+c$)	3·12	3·08	3·03	0·09
C(5)···H(5, $-c$)	3·14	3·18	3·10	0·04
H(4)···H(5, $-c$)	2·44	2·47	2·43	0·01
H(2)···H(3, $-c$)	2·52	2·50	2·49	0·03
H(3)···H(3′, $+b+c$)	2·57	2·55	2·51	0·06
H(2)···H(5, $-c$)	2·63	2·71	2·64	−0·01
H(1)···H(1′, $+a+c$)	2·67	2·62	2·53	0·14
σ_L(non-H)	0·005	0·004	0·003	
σ_L(one H)	0·03	0·02	0·02	
σ_L(H–H)	0·04	0·03	0·03	

Molecular structure

The bond distances and angles are given in Tables 5 and 6, respectively. Rigid-body librational corrections were applied by the method of Cruickshank (1961) using appropriate Gaussian-breadth parameters (Ito, Minobe & Sakurai, 1970). As can be seen from the Tables, the molecular dimensions are almost constant at the different temperatures; the average values with standard deviations are given in the last columns of the Tables and are also shown in Fig. 3.

The three-membered ring of the ethyleneimino group is approximately a regular triangle with bond angles of 61·2, 59·2 and 59·6°. The two N–C distances within the ring (1·475 and 1·469 Å) agree with the normal

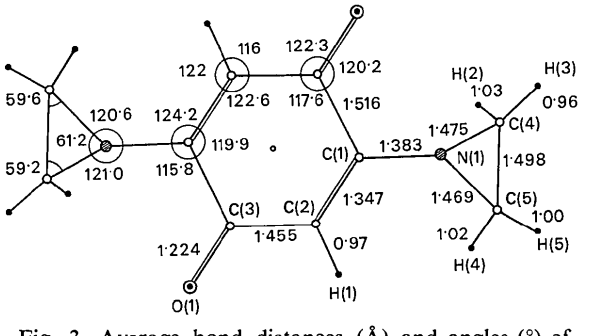


Fig. 3. Average bond distances (Å) and angles (°) of ethyleneimine quinone.

Table 5. *Bond distances* (Å)

The figures in parentheses are the librational corrections (positive). The σ_L in the lowest lines are the e.s.d.'s of the least-squares results. The σ in the last column are the composites of σ_L and the e.s.d.'s of the three sets of results.

	300° K	240° K	110° K	Average	σ
O(1)–C(3)	1·225 (1)	1·222 (1)	1·225 (0)	1·224	0·003
N(1)–C(1)	1·379 (1)	1·387 (1)	1·383 (1)	1·383	0·004
N(1)–C(4)	1·477 (3)	1·472 (3)	1·477 (1)	1·475	0·003
N(1)–C(5)	1·472 (3)	1·466 (3)	1·470 (1)	1·469	0·004
C(1)–C(2)	1·343 (4)	1·347 (2)	1·351 (1)	1·347	0·004
C(1)–C(3′)	1·520 (5)	1·517 (4)	1·510 (1)	1·516	0·004
C(2)–C(3)	1·448 (2)	1·460 (2)	1·456 (1)	1·455	0·005
C(4)–C(5)	1·494 (4)	1·499 (4)	1·500 (2)	1·498	0·004
C(2)–H(1)	0·95	0·97	0·98	0·97	0·02
C(4)–H(2)	1·05	1·03	1·01	1·03	0·02
C(4)–H(3)	0·93	0·98	0·96	0·96	0·03
C(5)–H(4)	1·04	1·02	0·99	1·02	0·03
C(5)–H(5)	1·02	0·98	1·00	1·00	0·02
σ_L(non-H)	0·004	0·003	0·002	0·003	
σ_L(C–H)	0·03	0·02	0·02	0·02	

Table 6. *Bond angles* (°)

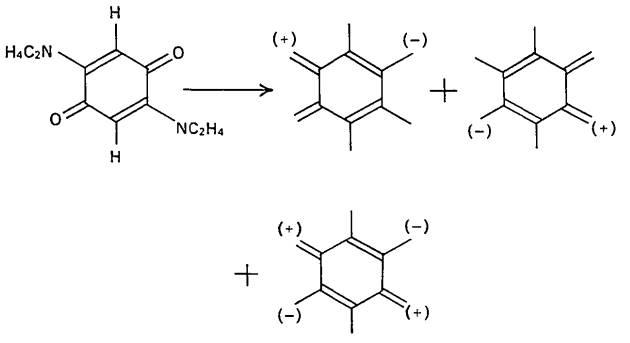
The librational corrections are not indicated because they were small (less than ±0·1). The σ_L are the e.s.d.'s of the least-squares results. The σ are the composites of σ_L and the e.s.d.'s of the three sets of results.

	300° K	240° K	110° K	Average	σ
C(1)–N(1)–C(4)	121·3	120·7	120·9	121·0	0·3
C(1)–N(1)–C(5)	120·8	120·6	120·5	120·6	0·2
C(4)–N(1)–C(5)	60·9	61·4	61·2	61·2	0·3
N(1)–C(1)–C(2)	124·3	124·1	124·1	124·2	0·2
N(1)–C(1)–C(3′)	116·1	115·7	115·5	115·8	0·3
C(2)–C(1)–C(3′)	119·4	120·0	120·2	119·9	0·3
C(1)–C(2)–C(3)	123·0	122·5	122·2	122·6	0·3
C(1)–C(2)–H(1)	122	123	121	122	1
C(3)–C(2)–H(1)	115	115	117	116	1
O(1)–C(3)–C(1′)	119·7	120·4	120·4	120·2	0·3
O(1)–C(3)–C(2)	122·7	122·1	122·0	122·3	0·3
C(2)–C(3)–C(1′)	117·6	117·5	117·6	117·6	0·2
N(1)–C(4)–C(5)	59·4	59·1	59·2	59·2	0·2
N(1)–C(4)–H(2)	118	116	116	117	1
N(1)–C(4)–H(3)	116	115	116	116	1
C(5)–C(4)–H(2)	117	118	118	118	1
C(5)–C(4)–H(3)	124	120	121	122	2
H(2)–C(4)–H(3)	113	116	115	115	2
N(1)–C(5)–C(4)	59·7	59·5	59·6	59·6	0·2
N(1)–C(5)–H(4)	116	116	117	116	1
N(1)–C(5)–H(5)	113	115	115	114	1
C(4)–C(5)–H(4)	117	116	118	117	1
C(4)–C(5)–H(5)	118	122	120	120	2
H(4)–C(5)–H(5)	119	116	115	117	2
σ_L(non-H)	0·3	0·2	0·1	0·2	
σ_L(one H)	2	1	1	1	
σ_L(two H)	3	2	2	2	

N–C single-bond distance (1·47 Å), whereas the C–C distance (1·498 Å) is significantly shorter than the single-bond distance (1·54 Å) (Pauling, 1960). These distances may also be compared with those of a free ethyleneimine molecule, N–C = 1·488 and C–C = 1·480 Å, determined by microwave spectroscopy (Turner, Fiora & Kendrick, 1955); the N–C and C–C distances of ethyleneimine quinone are 0·016 Å shorter and 0·018 Å longer, respectively, than those of the

ethyleneimine molecule. The H–C–H planes are approximately perpendicular (average 87·7°) to the three-membered ring. The observed H–C–H angles, 115 (2) and 117 (2)°, are significantly larger than the tetrahedral angle and are in good agreement with the theoretical prediction of 116° for cyclopropane (Coulson & Moffitt, 1949).

The observed dimensions of the quinone ring in ethyleneimine quinone are quite similar to those in similar crystals; for example, in chloranilic acid and chloranilic acid anhydrate, the average bond distances are: C=O = 1·225, C=C = 1·346, C–C = 1·506 and 1·446 Å (Anderson, 1967). It should be noted that the two C–C single-bond distances within a quinone ring in these crystals are significantly different; the differences are 0·061 and 0·060 Å in ethyleneimine quinone and chloranilic acid, respectively. However, in *p*-benzoquinone (Trotter, 1960) or in symmetrically substituted quinones such as tetrachloro-*p*-benzoquinone (Chu *et al.*, 1962), the two C–C distances are almost the same. As was pointed out by Anderson (1967) for chloranilic acid, this asymmetry of the C–C distances together with the short N(1)–C(1) distance (1·383 Å) shows that the following canonical forms are also important in ethyleneimine quinone:



The equations of the best-fit planes through the quinone rings are given by:

$$-0{\cdot}4452x-0{\cdot}4019y+0{\cdot}8967z=0 \ (300\,^{\circ}\mathrm{K})$$
$$-0{\cdot}4457x-0{\cdot}4012y+0{\cdot}8906z=0 \ (240\,^{\circ}\mathrm{K})$$
$$-0{\cdot}4487x-0{\cdot}3991y+0{\cdot}8865z=0 \ (110\,^{\circ}\mathrm{K})$$

where x, y and z are measured along the crystallographic cell edges in Å units. The maximum deviation of the ring carbon atoms is 0·051 Å. The oxygen and nitrogen atoms also lie approximately on these planes; the average deviations are 0·042 and 0·082 Å, respectively.

Bonding electrons and the bent bond

The equations of the ethyleneimino planes are given by:

$$-0{\cdot}1266x+0{\cdot}3742y+0{\cdot}8936z=2{\cdot}174 \ (300\,^{\circ}\mathrm{K})$$
$$-0{\cdot}1328x+0{\cdot}3844y+0{\cdot}8930z=2{\cdot}193 \ (240\,^{\circ}\mathrm{K})$$
$$-0{\cdot}1346x+0{\cdot}3867y+0{\cdot}8947z=2{\cdot}190 \ (110\,^{\circ}\mathrm{K}).$$

Difference electron density maps in these planes at the three temperatures are shown in Fig. 4. Although the peak values (from +0·06 to +0·26 e Å^{-3}) and peak positions are slightly different for different temperatures, three residual peaks always appear outside the triangle and approximately at the middle of each side.

If $\sigma(F_o)$ is assumed to be KF_o with K constant, the standard deviation of the electron density can be estimated from the equation

$$\sigma(\varrho)=K\left(\frac{p}{2\pi}\right)^{3/4}\left(\frac{1}{V}\sum Z^2\right)^{1/2}$$

where Z is the atomic number, V is the unit-cell volume, and p depends on the shape of the atom including the thermal vibration. With $K=4\,\%$, and $p=4$, 3 and 2 for each temperature, $\sigma(\varrho)$ is 0·05, 0·04 and 0·03 eÅ^{-3} at 300, 240 and 110°K. Since the majority of the residual peaks are more than twice these standard deviations, and also appear systematically at the different temperatures, they can be attributed to bonding electrons. The peaks are displaced from the sides of the triangles by 0·33 Å (average). The line joining a peak to each of the adjacent atoms is inclined 24° (average) to the internuclear line. Therefore, if we assume that the bond is directed from an atom to the adjacent residual peaks, the 'bent bond' is 108° instead of the highly strained angle of 60°.

These results are in fairly good agreement with those for *cis*-1,2,3-tricyanocyclopropane; the corresponding displacement and inclination angle are 0·32 Å and 22° respectively (Hartman & Hirshfeld, 1966). The result for tetracyanoethylene oxide (Matthews & Stucky, 1970) is not quite in agreement with the present result. In the ethylene oxide ring, although the residual electron density of about 0·45 e Å^{-3} appears at the outside of the C–C bond, the bend in the C–O bond is obscured by the tail off of the broad maximum near the centre of the ring. Such an accumulation of electron density at the centre of the ring is not observed in the ethyleneimine molecule.

Difference electron density maps through the quinone rings at the three temperatures are shown in Fig. 5. Residual peaks are observed on almost all internuclear lines. They are more pronounced with decreasing temperatures. In the plane of the ring, the peaks on the π-bonds are systematically lower than those of the σ-bonds. On the C=O double bond, there are no well-defined peaks; similar absence is also observed in 2,5-dimethyl-*p*-benzoquinone (Hirshfeld & Rabinovich, 1967), and in fumaramic acid (Hirshfeld, 1971).

Thermal vibrations

As can be seen from Table 2 and the last column of Table 1, the temperature factors of the atoms decrease systematically with decreasing temperatures. The mean-square amplitudes along the **c*** direction (U_{33}) are

significantly larger than those along the **a*** and **b*** directions (U_{11} and U_{22}); *i.e.* the atoms vibrate more out of the molecular sheet than within the sheet. This anisotropy of vibration is reflected on the anisotropy of thermal expansion of the crystal; the linear expansion coefficients within the range 300 to 110°K along the **a**, **b** and **c** directions are 61, 45 and 92×10^{-6}, respectively.

The anisotropic temperature factors of the atoms were transformed into the rigid-body vibration of the molecule by the method of Cruickshank (1956). The axes of molecular vibration were taken along the

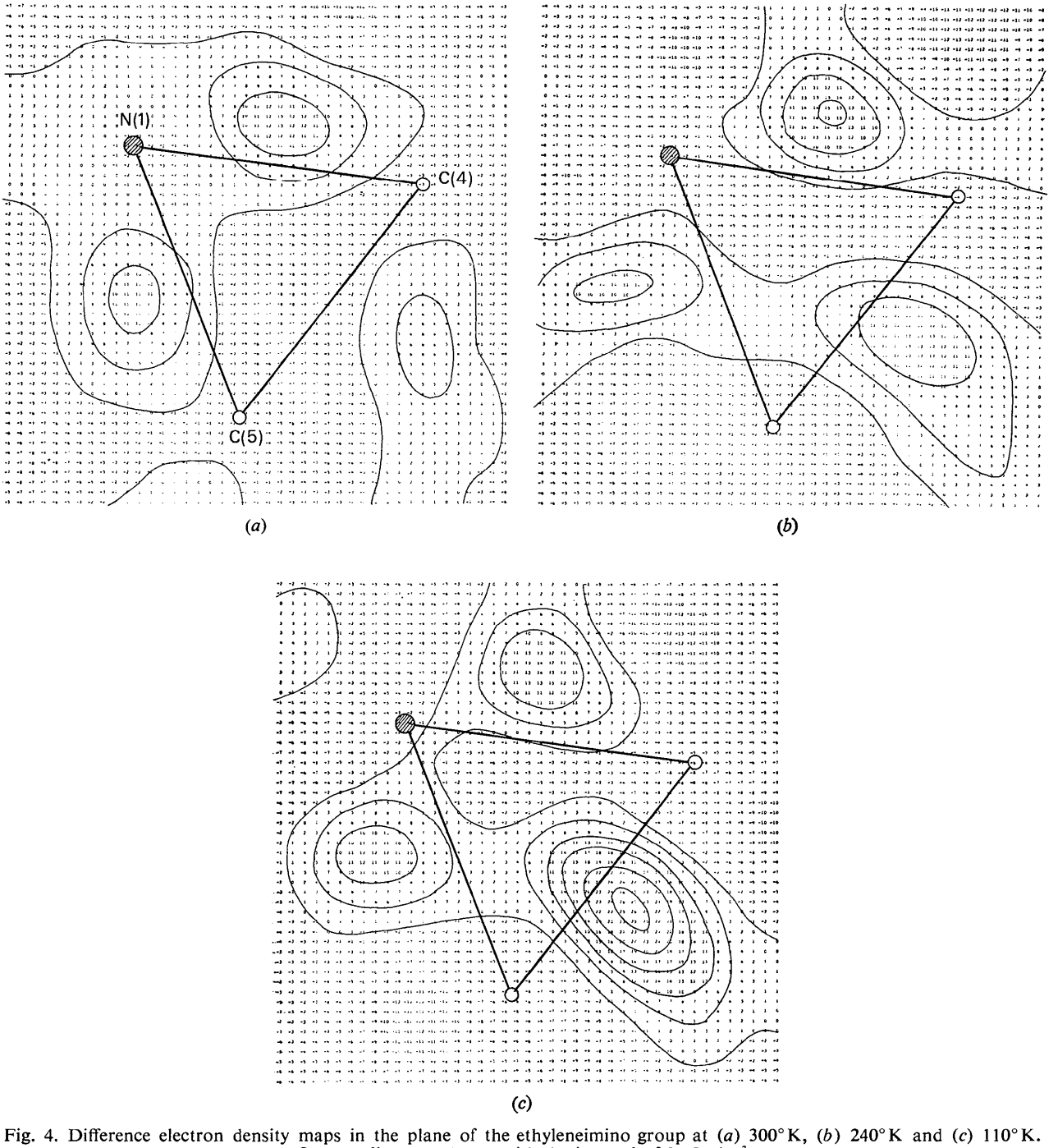


Fig. 4. Difference electron density maps in the plane of the ethyleneimino group at (*a*) 300°K, (*b*) 240°K and (*c*) 110°K. Contour lines are drawn with the interval of 0·05 eA^{-3}.

principal axes of the moment of inertia as shown in Fig. 6. The most probable values of the translational and librational tensors, T_{ij} and Ω_{ij} respectively, are given in Table 7. All non-hydrogen atoms were used for the calculations. The observed and calculated temperature factors of the individual atoms were in fairly good agreement; the average relative errors at 300, 240 and 110°K are 9·7, 8·1 and 11·0% respectively. It should be noted that as the temperature goes down from 300 to 110°K, the root-mean-square amplitudes of the translational and librational vibrations decrease to about one half of the original.

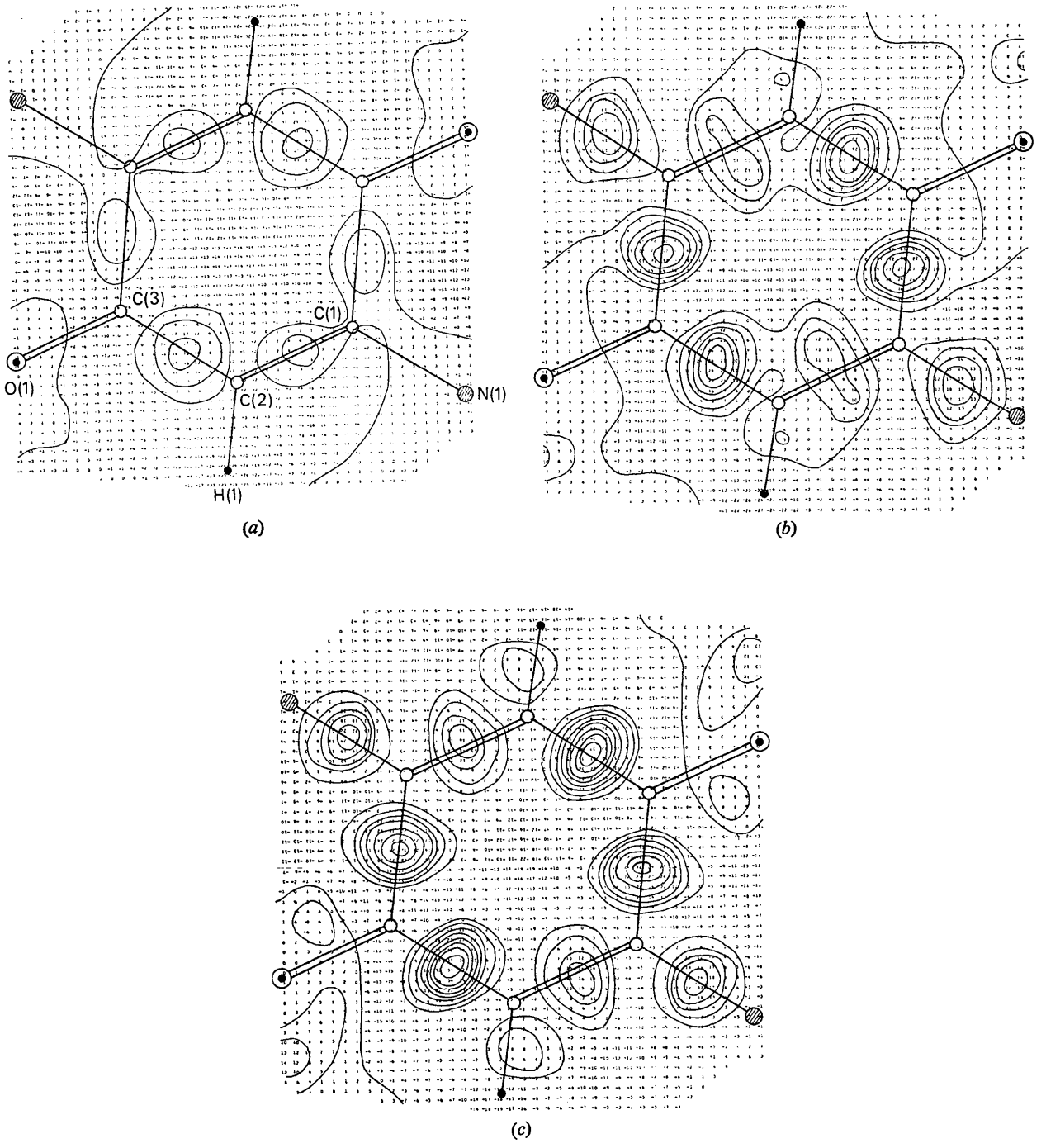


Fig. 5. Difference electron density maps in the plane of the quinone ring at (*a*) 300°K, (*b*) 240°K and (*c*) 110°K.

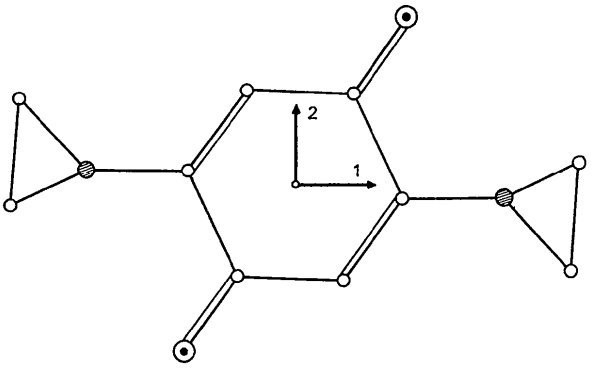


Fig. 6. Axes of the rigid-body vibration. Axis 3 is out of the plane of the paper.

Table 7. *Tensors of the rigid-body vibration and the root-mean-square amplitudes of vibration along the principal axes of the tensors*

The principal axes of the vibrational tensors, 1′, 2′, 3′ and 1″, 2″, 3″, are approximately parallel to those of the moment of inertia, 1, 2, 3, respectively.

	300° K	240° K	110° K
T_{11} (10^{-4} Å^2)	284 (8)	196 (5)	88 (3)
T_{22}	250 (10)	195 (7)	90 (4)
T_{33}	281 (15)	185 (9)	77 (5)
T_{12}	0 (8)	0 (5)	2 (3)
T_{13}	49 (8)	18 (5)	8 (3)
T_{23}	−3 (11)	−3 (7)	−4 (4)
$t(1')$ Å	0·182	0·145	0·096
$t(2')$	0·158	0·140	0·095
$t(3')$	0·153	0·131	0·085
Ω_{11} [10^{-1} (°)^2]	267 (17)	209 (11)	68 (6)
Ω_{22}	46 (5)	28 (3)	11 (2)
Ω_{33}	40 (5)	34 (3)	11 (1)
Ω_{12}	−10 (7)	5 (4)	3 (2)
Ω_{13}	8 (8)	3 (5)	1 (3)
Ω_{23}	−2 (4)	3 (3)	1 (2)
$\omega(1'')$ (°)	5·2	4·6	2·6
$\omega(2'')$	2·1	1·6	1·0
$\omega(3'')$	2·0	1·9	1·1

The numerical calculations were performed on the FACOM 270-30 computer of this Institute with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). This work was supported, in part, by the Science Research Grant of the Ministry of Education.

References

ANDERSON, E. K. (1967). *Acta Cryst.* **22**, 188–191.
BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc.* A**273**, 435–454.
BONACCORSI, R., SCROCCO, E. & TOMASI, J. (1970). *J. Chem. Phys.* **52**, 5270–5284.
CHU, S. S. C., JEFFREY, G. A. & SAKURAI, T. (1962). *Acta Cryst.* **15**, 661–671.
COULSON, C. A. & MOFFITT, W. E. (1949). *Phil. Mag.* **40**, 1–35.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.
CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–897.
FRITCHIE, C. J. JR (1966). *Acta Cryst.* **20**, 27–36.
GAUSS, W. & PETERSEN, S. (1955). *Angew. Chem.* **67**, 217–231.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
HARTMAN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20**, 80–82.
HIRSHFELD, F. L. (1971). *Acta Cryst.* B**27**, 769–781.
HIRSHFELD, F. L. & RABINOVICH, D. (1967). *Acta Cryst.* **23**, 989–1000.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.
International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
ITO, T. (1971). *Rep. Inst. Phys. Chem. Res.* **47**, 47–60.
ITO, T., MINOBE, M. & SAKURAI, T. (1970). *Acta Cryst.* B**26**, 1145–1151.
ITO, T. & SAKURAI, T. (1972). *Acta Cryst.* A**28**, S11.
KOCHANSKI, E. & LEHN, J. M. (1969). *Theoret. Chim. Acta* **14**, 281–304.
LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, p. 288. London: Bell.
MATTHEWS, D. A. & STUCKY, G. D. (1971). *J. Amer. Chem. Soc.* **93**, 5954–5959.
PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
SAKURAI, T., ITO, T. & IIMURA, Y. (1970). *Rep. Inst. Phys. Chem. Res.* **46**, 82–99.
SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62–69.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TROTTER, J. (1960). *Acta Cryst.* **13**, 86–95.
TURNER, T. E., FIORA, V. C. & KENDRICK, W. M. (1955). *J. Chem. Phys.* **23**, 1966.